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VARIATION IN THE NIGHT ATMOSPHERE

OF THE MEAN MOLECULAR WEIGHT OF THE AIR IN THE

100 TO 210 KM ALTITUDE RANGE

ACCORDING TO MASS-SPECTROMETRIC MEASUREMENTS

by

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(Ob izmenenii sprednego milekulyarnogo vesa vozdukha
v nochnoy atmosfere na vysotakh ot 100 do 210 km po
mass-spektrometricheskim izmereniyam)

Direct measurements of gas content are of paramount
value when determining the thermodynamic parameters of the
atmosphere above 100 km and studying their variations as a
result of various effects changing the state of the atmosphere.
One of the most important results obtained during these measu-
rements are the data on relative concentrations of the beasic
atmospheric components determining the value of the mean mole-
cular weight at considered altitudes.

Data on the investigation of neutral gas content in
the 100 — 210 km altitude range, carried out in July 1959 in
the middle latitudes of the European SSSR in morning hours
[1, 2], allowed a unilateral conclusion on the mean molecular
weight variation of only the gas inside the mass spectrometer's
analyzer. In order to estimate the variation with altitude of
the mean molecular weight of gases in the atmosphere, it is
necessary to take account the variation of analyzed gases'
content in the inlet nozzle and in the analyzer itself.

If the distance from the inlet opening to the ion source is significantly greater than the former's diameter ($l/d > 1$), as was the case in the experiments of [3, 4], only an insignificant part of molecules outflowing from the total flux entering the a alyzer reaches the ion source without colliding with the walls and in the screen of the analyzer. There is naturally a substantial probability of variation of analyzed gas' content and particularly of its atomic chemically-active component which may partly recombine or enter into combination with the material of the walls and of the screen of the analyzer.

The effect of recombination on the quantitative measurement of atomic oxygen concentration was noted in the earlier works by Meadows and Townsend [3], and also in the works [1, 2]. The possibility of quantitative measurements of relative atomic oxygen concentrations with the aid of mass-spectrometers was questioned in the works by Johnson [5] and Istomin [6], on account of recombination and combining reactions in the analyzer. According to mass-spectrometric measurements [1, 2], atomic nitrogen content in the indicated altitude range is not more than 1 to 2 percent of the molecular, and thus cannot exert any significant effect on the value of the mean molecular weight of the air at these altitudes. Therefore the quantitative accounting of the decrease inside the analyzer of atomic oxygen concentration has a determining value for the computation of the mean molecular weight at these altitudes. Another factor, changing analyzed gases' content in the fast-moving analyzer is the selection by masses [7], which diminishes the relative light gas content in the reflected stream. For the case when only the reflected stream is ionized in the mass-spectrometer's analyzer, this stream being in thermal equilibrium with the walls, the selection factor by masses for O_1 according to Repnev data [7], is equal to $\mu_0 = 1.323$. For the obtention of relative O_1 concentration in the atmosphere this coefficient must be multiplied by the

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maximum contraction of the length of the inlet nozzle and increase of its diameter (Fig.1). The main technical characteristics of the mass spectrometer applied are presented below.
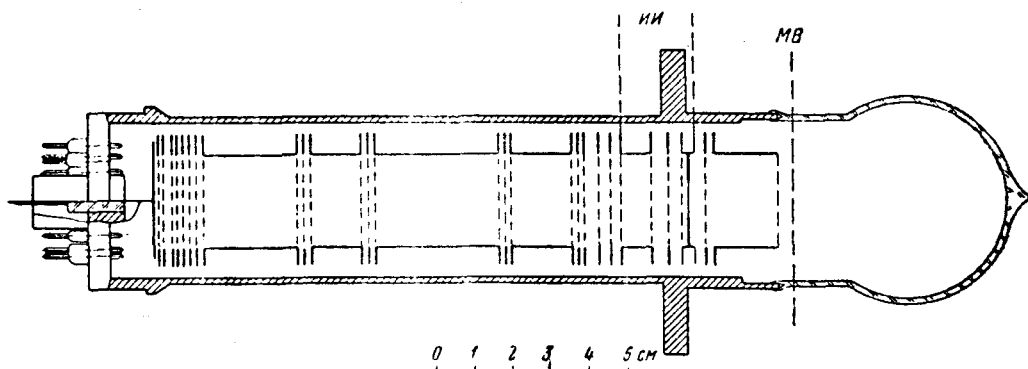
Fig.1. Scheme of the A2 analyzer (1960 experiment).
— ion source ; MB — place of analyzer's opening.

1. Mass range (in atomic units of mass): 1 $\rightarrow$ 4.12 $\rightarrow$ 60.

2. The resolving power $\dfrac{M}{M}$ in the region 40 a.e.m. is 45.

3. The partial sensitivity for argon is 5 10^{-10} mm Hg col. (os cillograph reading for the minimum registered current of 4 10^{-14} a.)

4. Duration of mass scan cycle 3 sec.

5. Dynamic range of the ion current amplifier — 2.2 10^{4}.

6. Consumed power at feed voltage of 27.5 v — 4 watt.

7. Weight of the device — 2 kg.

To control the operation of the device and the calibration by masses, the mass spectrometer's analyzer was filled with a mixture of control gases (H_2, He, Ne and Ar) up to a pressure of 1 10^{-5} mm. Hg. col.

The mass spectrometer was installed in a small hermetized container (Fig. 2), which in its turn was fastened on a revolving bracket in a special nest of one of the compartments of the retrieveable geophysical container. This container was raised to great heights

with the aid of a large geophysical rocket, and separated from it moving away to a distance of several hundred meters. Upon separation from the rocket on signal from the automatic timer the device and the galvanometer oscillograph were switched on, and during 20 sec prior to analyzer opening registration of control gases' spectra took place. By the moment of analyzer opening the small container, revolving on the bracket and emerging from the nest, settled into a position at an angle of 45° between the axis of the analyzer and the longitudinal axis of the large container (Fig. 3). The opening of the mass spectrometer was made with the help of a special knife on command from the automatic timer. After opening, the knife settled in the most remote position from the inlet opening of the analyzer. During the flight of 23 September 1960, 50 mass spectra were obtained at ascent, and 51 at descent of the container, covering the 100 to 210 km altitude range.

From the informations obtained on the composition of the air in the indicated altitude range examined are in the current work data on relative concentrations and their variations with height only for the main atmospheric components determining the mean molecular weitht of the air. The other results, including those concerning the gravitational separation of gases and the contents of small admixtures will be examined in another paper.
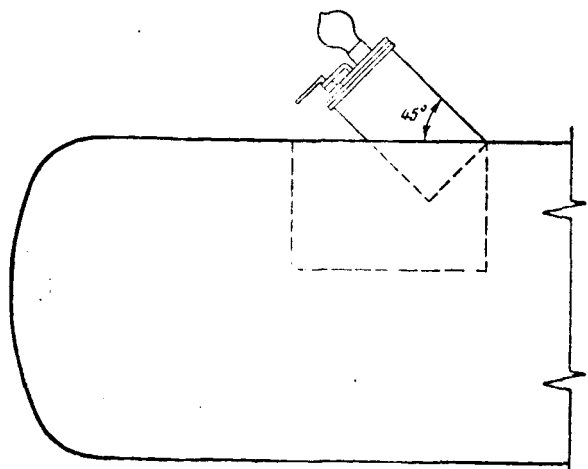
For the quantitative appraisal of the decrease of atomic oxygen in the analyzer we compared the relative concentrations of O_1 and N_2 by the results of two experiments conducted with analyzers of different construction.

In one of them (1959 experiment ref. [1, 2]), the direct hitting of the ionizing

region by atmosphere atoms and molecules was excluded on account of the peculiar construction of the ion source, and of the long inlet nozzle. In that case oxygèn atoms , entering the analyzer, underwent a substantial number of collisions before reaching into the ionizing region of the ion source, and thus the recombination in the entering flux differed little from that in the reflected flux.

The ion current of the atomic oxygen registered by the analyzer may be represented in the form of the sum of two currents:

$$I = I_{ent,} + I_{refl}.$$

where I_{ent} is the ion current appearing because of ionization of the enterring stream , and I_{refl} is the ion current from the ionization of the reflected (outgoing) stream of atomic oxygen. It is obvious that $I_{refl} < I_{ent}$ (this inequality corresponds to the decrease in atomic oxygen concentration in the reflected stream.). If we assume that in an analyzer similar to the Al-type used in 1959 the recombination is absent in the entering stream, the inequality $I_{refl} < I'_{refl} < I_{ent}$, where I'_{refl} is the ion cur-rent from the ionization of the reflected stream in an hypothetical analyzer with absence of recombination in the entering stream, $\frac{valid}{is}$ for a real analyzer Al. Consequently, it would be a great error to assume that in the analyzer Al the ion current I is equal to the doubled ion current I'_{refl} that corresponds to the ionization of the reflected stream in the hypothetical analyzer Al:

$$(I_{refl} + I_{ent} = 2 I'_{refl})$$

Analyzer A2, shown in Fig.1, and corresponding to the 1960 experiment, appears to be close to the hypothetical analyzer Al as far as its construction is concerned. Owing to the short nozzle and a great diameter for the inlet opening, atomic oxygen recombi-nation in the entering stream was reduced to a minimum, and was

in any case much less than in the reflected stream. In this experiment the variation in the orientation of the inlet opening of the analyzer relative to the incident flow did not cause any significant variations in the ion currents' O_1 and N_2 ratio, which also points to the insignificant role of the recombination in the entering flow. In the opposite case, and because I_{ent} represents the prevailing part of the total ionic current, the variations of this ratio would be notable and they would correlate with the variation of the orientation, which was not observed in the conducted experiment. Consequently, there is sufficient basis for neglecting the recombination in the incident flow, and to estimate that the ionic current I_{ent}, forming in the course of the ionization of the entering flow, corresponds to the concentration of O_1 in the undistorted atmosphere. In that case, the factor

$$k = 2I_{ent} : (I_{refl} + I_{ent})$$

will characterize the correction for the determination of the undistorted concentration of atomic oxygen. To determine that factor it is necessary to find the correlation between the components I_{ent} and I_{refl} of the total ionic current.

Comparison of the two experiments has shown that the relative concentration of atomic oxygen at all altitudes is about four times greater according to measurements with the A2 analyzer than to those with the A1 analyzer.

Assuming that a) the relative concentration of atomic oxygen in the atmosphere is identical in both experiments and b) that the degree of decrase of atomic oxygen concentration in the reflected stream is identical for both analyzers — A1 and A2, one may compose a system of two equations for the determination of the corrective factor k (the current values being taken in conditional units):

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$$2\,I'_{refl} = 1 \text{ (for the A1 analyzer)} \qquad (1)$$

$$I_{enter} + I'_{refl} = 4 \text{ (for the A2 analyzer)} \qquad (2)$$

Hence we find the value k = 1.75, characterizing the correction
for the determination of atomic oxygen concentration in the analy-
zer A2. The thus obtained corrective factor takes into account the
recombination, selection by masses and the possible combination
reactions of atomic oxygen with the material of analyzer's walls.

One must however examine to what extent the non-fulfilment
of confitons A) and b) may change the value of the factor k.
Condition a) assumes that the ratio of atomic oxygen to molecular
nitrogen concentration in the atmosphere in the 100 to 210 km alti-
tude rangee in the 1959 experiment conducted in July at sunrise [1, 2],
is equal to the corresponding ratio in the 1960 experiment, carried
out in September at 00 56 hours local time. Both experiments were
conducted at more or less the same latitude and about 7 hours after
sunset. Thus, the possible difference in the value of the concen-
tration ratio may only be linked with seasonal factors — a more
prolonged effect of the Sun upon the atmosphere in July (17 hours)
in comparison with September (12 hours). Bearing in mind that the
recombination reaction rates are rather small [9], one may assert
that the relative concentrations of atomic oxygen differed more than
twice in both experiments. Even for the case when the relative O_1
concentration in July 1959 is more than double that in September 1960,
the value of the factor k varies only from 1.75 to 1.87.

But the non-fulfilment of the condition b) may exert a more
substantial effect on the value of the factor k. This condition con-
cerns the identity of O_1 concentration decrease in the reflected
stream for two different analyzers. In fact, for an identical dia-
meter and the same amount of cascades and screens the A1 analyzer
has a length twice as great as that of the A2 analyzer. It is na-
tural that the probability of atomic oxygen recombination in the

reflected stream is greater for the lon analyzer than for the short one. For the case, when the ionic current from reflected flux ionization in the A2 analyzer exceeds twice the corresponding current in the A-1 analyzer, the corrective factor will be 1.5. That is why the factor $k = 1.75$, obtained fron equations (1) and (2) is factually the upper limit for the value of the corrective factor in the A2 analyzer. Taking the above-said into account, we shall admit the $k = 1.60 \pm 0.25$ for the corrective factor, where the component ± 0.25 accounts for the possible inaccuracy connected with the assumptions made.
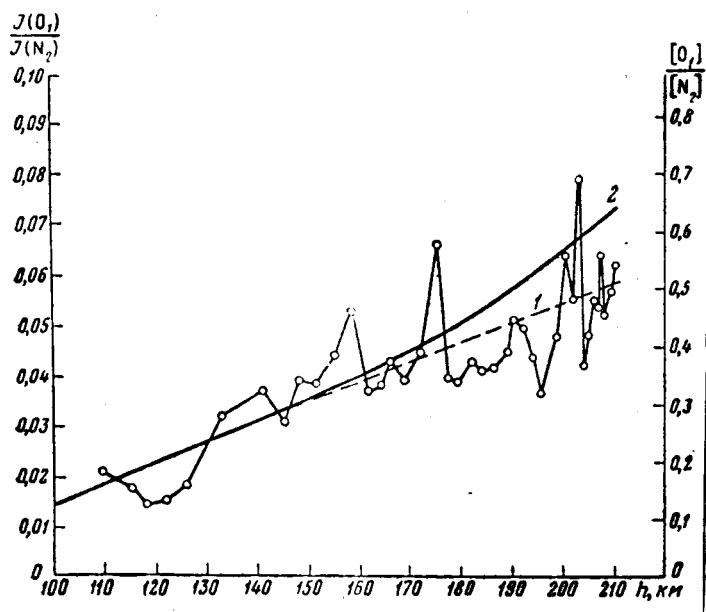

Fig. 4. Variation with height of the concentration
ratio of O_1 and N_2 :

1 — curve, traced through the experimental points;
2 — the same curve with the correction for the effect of N_2 separation ; the left scale is the ionic currents'ratio, and the right scale is the ratio of concentrations.

Utilizing the obtained value of the factor, we may determine the concentration of atomic oxygen in the atmosphere.

To do that we must increase k times the concentration measured
by the mass-spectrometer. Accounting for all the corrections,
the conducted examination provides the possibility of maling the
following conclusions relative to the basic composition of the
air and the variation of its separate components for altitudes
from 100 to 210 km.

The main components in the indicated altitude range are
the molecular nitrogen, atomic and molecular oxygen. At the same
time, the molecular nitrogen continues to remain the prevailing
component through to maximum heights (210 km), just as was the
case in the 1959 experiment [1, 2].

Atomic nitrogen content in the atmosphere at these alti-
tudes does not exceed 2% of the molecular nitrogen concentration,
which confirms former mass-spectrometric measurements [1, 2].
Consequently, processes, owing to which notable amounts of atomic
nitrogen accumulation would have taken place, do not play an essen-
tial role at these altitudes.

As may be seen from Fig. 4, the relative concentration with
height of atomic oxygen increases by about 5 times, and constitutes
nearly 65 ±20% of the molecular nitrogen concentration.

The relative concentration of molecular oxygen (Fig. 5) at 100
km is about equal to that in the surface (near the ground) layer.
It diminishes by about 50% with altitude increase and at 210 km it
constitutes about 14 ± 6% of the concentration of molecular nitrogen.
The concentration of molecular oxygen is determined with the account-
ing of recombination inside the analyzer in the assumption that all
the atomic oxygen outflowing from the entering and reflected streams
is transformed into molecular oxygen because of interaction with the
surface of the analyzer.

On the basis of the data obtained, we computed the distribution of the relative concentrations of the three atmospheric constituents as shown in the diagram of Fig. 6, and also the value of the mean molecular weight in the 100 to 210 km altitude range (see Fig. 7). The possible deflections from the computed values, on account of errors in the determination of concentrations of the basic atmospheric constituents, constitute near 2% at 100 km, and increase almost linearly with height to 4% at 210 km.
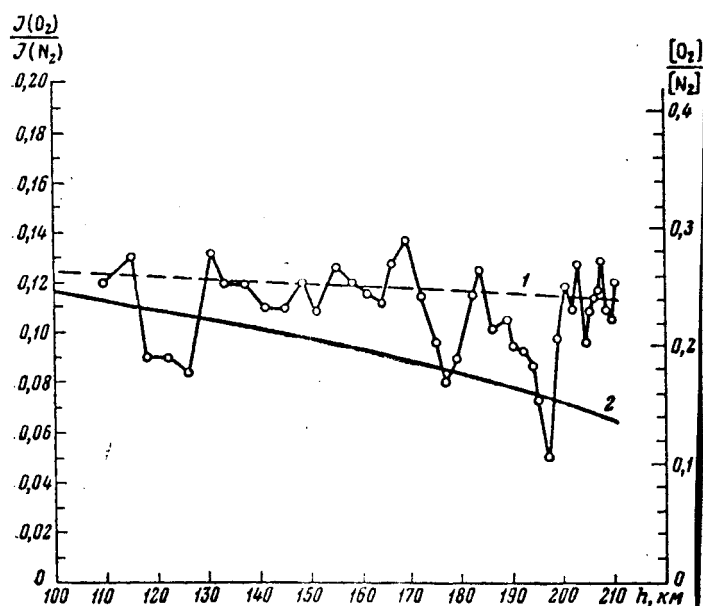

Fig. 5. Variation with height of the ratio
of O_2 to N_2 concentrations :

1 — curve traced through the experimental points
2 — same, with correction for O_1 recombination
   in the analyzer. The left scale is the ionic
   currents' ratio, the right hand scale — ratio
   of concentrations

From the data obtained, we may also compute the degree of dissociation of molecular oxygen at various heights $d(O_2)$.

The computation was made according to formula

$$d(O_2) = \left[1 - \frac{n(O_2)}{0.21 n(M)}\right] \cdot 100\%$$

where $n(O_2)/n(M)$ is the ratio of concentration of O_2 to the total concentration of the main atmospheric constituents. The results brought out below, account being taken of possible deflections, show the rise of the fraction of dissociated oxygen with height.

h, км.....	100	110	120	130	140	150	160	170	180	190	200	210
$d(O_2)$, %...	14 ± 11	91 ± 11	24 ± 11	27 ± 11	31 ± 11	36 ± 12	40 ± 12	45 ± 13	49 ± 14	54 ± 14	59 ± 15	63 ± 1

It may be seen from these data that there still is a significant quantity of molecular oxygen at 210 km, which must be evidence of significant effect of diffusive mixing processes at these heights.
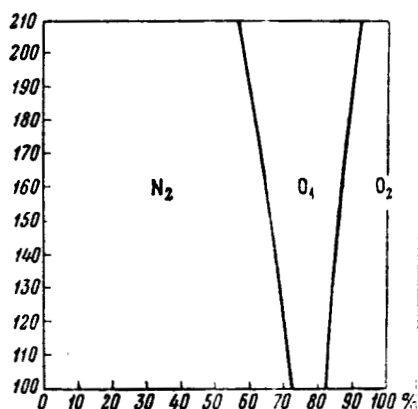

Fig. 6. Diagram of the distribution of relative concentrations with height of N_2, O_1 and O_2.
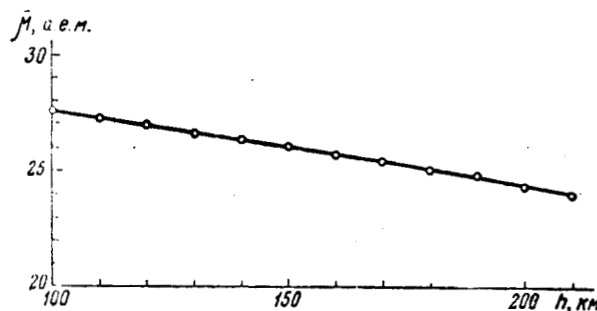

Fig. 7. Variation of the mean molecular weight of the air as a function of altitude.

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